POSITION PAPER

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The case for a large natural source of TFA in the oceans is extremely strong, well- documented, and scientifically supported.

The large body of scientific data shows that anthropogenic sources are not responsible for the majority of TFA in the oceans

The generally accepted conclusion is that trifluoroacetate (TFA) does occur naturally, in part based on the undisputed large quantities of TFA in the oceans. Surprisingly, the recent review paper "Insufficient evidence for the existence of natural trifluoroacetic acid" by Joudan et al[1] concludes that "*the presence of TFA in the deep ocean and lack of closed TFA budget is not sufficient evidence that TFA occurs naturally, especially without a reasonable mechanism of formation.*" However, there are some obvious errors in the Joudan et al review and the review questions the accepted large body of scientific evidence for the natural occurrence of TFA.

Natural TFA Burden in the Oceans

Frank[2] and Scott[3] measured TFA concentrations in good agreement in similar locations. The difference in derived total burden (Frank, 268 million tonnes, Scott 61–205 million tonnes) in the oceans results from Scott having a more comprehensive set of TFA measurements for depth profiles and the different oceans. Scott collected a series of depth profiles at 22 sites in the Arctic, North and South Atlantic, and Pacific Oceans to determine spatial patterns for trifluoroacetate (TFA). The Joudan et al paper accepts that there is a large quantity of TFA in the oceans but suggests that there is uncertainty in this quantity, which is why Scott calculated a range (61–205 million tonnes) to take into account the uncertainty. Joudan et al discussed the analytical method of Frank noting that "The authors were very thorough in quality control measures during their sampling". Joudan et al, when discussing Limit of Detection and field blanks, would not be aware that rigorous 'round robin' TFA and blank analyses[4] were carried out, by Frank (University of Bayreuth) and the University of Nevada, which carried out studies on TFA concentrations in precipitation in California and Nevada in the same period.[5]

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[1] S. Joudan, A. O. De Silva and C. J. Young, Insufficient evidence for the existence of natural trifluoroacetic acid Environmental Science Processes & Impacts October 2021 DOI: 10.1039/d1em00306b

[2] H. Frank, E. H. Christoph, O. Holm-Hansen and J. L. Bullister, Trifluoroacetate in ocean waters, Environ.Sci. Technol., 2002, 36(1), 12–15.

[3] B. F. Scott, R. W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer and D. C. G. Muir, Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans, Environ. Sci. Technol., 2005, 39(17), 6555–6560.

[4] This independent work was funded as part of an AFEAS contract, with the final report issued to AFEAS in 2000.

[5] Determination of Trifluoroacetic Acid in 1996-1997 Precipitation and Surface Waters in California and Nevada, C. Wujcik, T.M. Cahill, and J.N. Seiber, Environ. Sci. Technol. 1999, 33, 1747-1751.

The Scott oceanic burden range calculation approach provides maximum and minimum estimates of the TFA inventories in the major ocean basins. For the Pacific Ocean, values measured to depths down to 4000 m have been used, but the lower 5000 m of the depth has been given a minimal value of 10 ng/L and a maximum value of 175 ng/L. The maximum value for the Atlantic Ocean is calculated by assigning the entire water column a TFA concentration of 175 ng/L. The minimum value is derived by assigning the upper 4000 m a TFA concentration of 175 ng/L and deeper waters, a value of 10 ng/L. The TFA estimates for the Indian Ocean are derived by assuming the entire water column has either a maximum concentration, similar to the Atlantic Ocean, or minimum concentration, similar to the Pacific Ocean.

A similar approach (to Scott) has been used to develop an ocean inventory for C_4- C_{14} PFAS[6] however, in contrast to TFA, these substances do not occur naturally. The ocean inventory for each of these PFAS substances is in the range of about 1000 to 15000 tonnes, in contrast to the 61- 205 million tonnes of TFA estimated by Scott.

TFA found in the deep Arctic Ocean

Scott oceanic TFA concentration measurements included the Canadian Basin (western Arctic Ocean) deep or bottom waters. At 3000 m depth in the Canadian Basin of the western Arctic Ocean TFA concentration was measured as 160 ng/L similar to the concentrations measured in the Atlantic. **Joudan et al commented that** *"A limitation of these studies [Frank and Scott] was that they did not consider plausible TFA delivery mechanisms from ocean depths representing modern times to the deep ocean."* There have been a number of studies that discuss the Canadian Basin water stratification and water age. The Canada Basin is 3500–3800m deep and the 500–1000m thick deep temperature minimum layer (DTML) overlies the Canada Basin bottom water with the boundary at about 3000m between DTML and the bottom water.[7] Another paper[8] concluded that "observations have allowed us to speculate that **ongoing renewal of the deep Canada Basin is unlikely and the most likely scenario is that the present Canada Basin deep water is the result of a renewal event in the past**." An earlier paper concluded that the average age of the Canadian Basin Deep Waters is comparably high at perhaps 400 years.[9]

PFAS were not found in the deep Arctic Ocean. Joudan et al discussed PFAS profiles in ocean sampling to suggest that similar processes could account for TFA in deep ocean waters. However, for the Arctic Ocean, a recent paper not referenced by Joudan et al, "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean"[10] determined that PFAS (note the study did not include TFA so does not contradict the Scott measurements) were not found at depths below 250 m in the Arctic Ocean. "The

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[6] OECD Environment, Health and Safety Publications Series on Risk Management No. 30, 2015, Working towards a global emission inventory of PFASs: Focus on PFCAs- status quo and the way forward.

[7] Inferring Circulation and Lateral Eddy Fluxes in the Arctic Ocean's Deep Canada Basin Using an Inverse Method, H. V. Dosser and M-L Timmermans, Journal of Physical Oceanography, 2018 vol. 48 page 245, DOI: 10.1175/JPO-D-17-0190.1

[8] Evolution of the Deep Water in the Canadian Basin in the Arctic Ocean, M-L Timmermans and C. Garrett, Journal of Physical Oceanography 2006 vol. 36 page 866

[9] The arctic ocean component in the Greenland-Scotland overflow, B Rudels and D Quadfasel, International Council for the Exploration of the Sea paper C.M. 1991/C:30

[10] L.W.Y. Yeung, C. Dassuncao, S. Mabury, E.M. Sunderland, X. Zhang, R. Lohmann, Vertical profiles, sources, and transport of PFASs in the Arctic Ocean. Environ. Sci. Technol. 2017, 51 (12), 6735−6744.

detection of PFASs in the four depth profiles was limited to the 150 m below the surface, except for the North Barents Sea where a PFAS was detected down to 250 m below surface." Samples were taken at depths down to 3000 m[11] "*Deep layer water samples (3000 m depth from 4 different stations) were served as field blanks and were found below limits of quantification*". The paper states that the lifetime of tracers in Arctic Deep water is about 75 – 300 years.

The absence of PFAS at depths below 250 m, the lifetime of tracers in deep water and the high average age of the Canadian Basin deep waters all suggest that it is difficult to envisage a plausible TFA delivery mechanism representing modern times for anthropogenic TFA to account for the 160 ng/L concentration (similar to the Atlantic Ocean concentration) measured at 3000 m close to the boundary of the thick deep temperature minimum layer (DTML) and the Canada Basin bottom water.

Transport mechanisms to deep water

Joudan et al propose transport mechanisms to account for TFA in the deep ocean and compare TFA, PFAS and POPs in the deep ocean: *"This variability is consistent with more recent analysis of PFAS profiles in ocean sampling across extensive latitudinal gradients."* However, the paper "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean", discussed earlier, did not find PFAS below 250 m. If TFA and PFAS have similar transport mechanisms then it might be expected that PFAS would also have been found in the deep waters of the Arctic Ocean. Joudan et al compared TFA and PFAS depth profiles for the North Atlantic which will both be influenced by the meridional overturning circulation. However, the mid-Atlantic depth profiles show marked differences for PFAS and TFA. Frank measured TFA concentrations in the mid-Atlantic that were effectively uniform between the surface and 4150 m depth (190 to 210 ng/L at 8 different depths[12]). In contrast, Yamashita[13] found that for PFAS in the mid- Atlantic "*In each of the three Mid-Atlantic water columns, there was a considerable difference in PFAS concentrations between the surface and middle layers of the water column, below 800 m. Concentrations of PFAs were almost negligible in the deepest layers, below 4000 m. The latter finding suggests a lack of direct vertical transport of PFAs from surface to bottom waters*." Similarly, Yamashita comments that for the Labrador Sea, "*approximately 1% of the total emissions of PFOA has been transferred into the deep sea water over the past 60 years. At this rate of distribution, more than 4500 years would be needed for transfer of all of the current emissions of PFOA into the deep sea water in the Labrador Sea."*

In addition, the paper "Vertical Profiles, Sources and Transport of PFASs in the Arctic Ocean" also comments that results for PFAS contrast with vertical profiles of PCBs and PBDEs in the Arctic Ocean indicating vertical transport processes are weaker and potentially irrelevant for PFAS, as suggested by some modeling work. This transport mechanism, also discussed by Joudan et al, should also be irrelevant in the Arctic Ocean for TFA as it is highly hydrophilic in contrast to hydrophobic POPs, which partition readily to organic carbon and suspended particles, and particle settling has been suggested to be a dominant transport pathway to deeper water layers for these substances.

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[11] The deep water samples were from another area of the Arctic Ocean- the Nansen and Amundsen Basins.

[12] The depths (m) and concentrations (ng/L) measured are 0 m, 190 ng/L; 2, 200; 40, 210; 120, 205; 380, 210; 1000, 205; 4000, 195; 4150, 200;

[13] N. Yamashita, S. Taniyasu, G. Petrick, S. Wei, T. Gamo, P. K. S. Lam and K. Kannan, Perfluorinated acids as novel chemical tracers of global circulation of ocean waters, Chemosphere, 2008, 70, 11589–11609.

Therefore, the mechanisms proposed by Joudan et al could only explain a tiny fraction of TFA measured in the deep ocean, if any at all.

Anthropogenic sources of TFA

Anthropogenic sources of TFA have been reviewed in the 1990s. The 1999 Environmental Risk Assessment of trifluoroacetic acid (TFA)[14], not referenced by Joudan et al, was undertaken to determine the potential effects of TFA, formed from some HFCs and HCFCs introduced as new substances in the early 1990s. The Risk Assessment, which was published before the Scott and Frank ocean measurements, concluded that *"Surprisingly, environmental measurements in many of diverse locations show existing levels of 100 to 300 ng/l in water with one site (Dead Sea) having a level of 6400 ng/l. These levels cannot be accounted for based on current atmospheric sources and imply a long-term, possibly pre-industrial source."*

Other anthropogenic sources of TFA emissions were discussed in the Risk Assessment, including TFA production and use, by-product from hexafluoropropylene oxide production and anaesthetics. Another paper[15] considered and looked for TFA from a range of anthropogenic sources, in addition to HFCs and HCFCs, including, anaesthetics, pesticides, fluoropolymer waste incineration and the aluminium industry. More recent sources of TFA such as HFOs raised by Joudan et al are not relevant to the oceanic burden from concentration measurements undertaken by Frank (1998/1999) and Scott (1998/1999/2002).

Measurements for pre-industrial TFA

Joudan et al commented critically on several scientific papers, in particular a paper by von Sydow.[16] **S**ome of these comments cannot be substantiated and **Joudan et al is mistaken** about the quality of the analytical method employed by Von Sydow.

The von Sydow paper concluded ***"we confirmed the preindustrial presence of significant background concentrations of trifluoroacetate in historic precipitation samples from the analysis of firn"*** reporting TFA concentrations of 6–56 ng/l in 190 year-old Antarctic firn (crystalline or granular snow that has not yet been compressed into ice). The paper explains that "*on-site contamination and erroneous dating of the TFA detected in firn are highly unlikely. Major volcanic eruptions, such as that of Tamborain 1815, produced very distinct signals in the electrical conductivity measurements (ECM) used to date the Antarctic firn collected at different depths. This has two important implications for our study. First, it demonstrates that the dating of the sampled firn layers is reliable. Second, it shows that ions are practically immobile in permanently frozen Antarctic firn. Such low mobility must apply to TFA as well, because this compound exists as a salt at the pH values that prevail in firn (the pKa value of TFA is 0.2). In particular, our data indicate the following: (i) the TFA detected in the deepest part of the firn core must have been of preindustrial origin, and (ii) any contaminants that may have*

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[14] Boutonnet et al, 1999 Environmental Risk Assessment of trifluoroacetic acid, Human and Ecological Risk Assessment, February 1999, DOI: 10.1080/10807039991289644

[15] A. Jordan and H. Frank, Trifluoroacetate in the Environment. Evidence for Sources Other Than HFC/HCFCs, Environ. Sci. Technol. 1999, 33, 522-527

[16] L. M. von Sydow, A. B. Grimvall, H. B. Bor´en, K. Laniewski and A. T. Nielsen, Natural background levels of trifluoroacetate in rain and snow, Environ. Sci. Technol., 2000, 34(15), 3115–3118.

reached the surface of the sampled firn segments were efficiently avoided by drilling an inner core." **Joudan et al suggests** *"that there were problems in the dating methods used to assign age"* but does not offer any explanation why the results are in error except that three other papers did not find TFA in pre-industrial freshwater.

In addition, the von Sydow paper DOES have very good analytical method quality. Joudan et al is mistaken in stating for the von Sydow paper that *"Closer scrutiny of the reported analytical methods indicates flaws based on the first principles of quantitative analysis. All sample concentrations were extrapolated below their lowest calibration standard, which was 100 ng TFA into 10 mL water, resulting in a final concentration of 1000 ng mL^{-}1 after sample processing."* It is assumed that this statement also contains a typing error as 100 ng TFA in 10 ml of water is 10,000 ng/L. Table 1 explains how the analytical samples were prepared as reported in the paper. The TFA in the snow samples were concentrated to ensure that the final concentration was appropriate for the analytical instrument. Clearly it is incorrect to state that all sample concentrations were extrapolated below the calibration standard as the lowest calibration standard is equivalent to 2 ng/L for a 1000ml sample.

Table 1: Explaining the von Sydow analytical sample preparation and calibration

Samples to be analysed		**Concentration of prepared samples**
Snow or ice volumes 200 to 1000 ml	Assume 1000 ml	Evaporated and derivatisation and extraction into 100µl toluene and 100µl hexane (total 0.2 ml)
Assume 10 ng/L TFA concentration in snow sample	TFA quantity in the snow sample 10 ng	TFA derivative concentration in toluene/hexane is equivalent to 50,000ng/L
Assume 2 ng/L TFA in snow	TFA quantity 2 ng	TFA derivative concentration 10,000 ng/L
Calibration samples TFA in Milli-Q water (3 duplicates of each)		**Concentration of calibration samples**
0 ng in 10 ml water		0
100 ng in 10 ml water		10,000 ng/L
200 ng in 10 ml water		20,000 ng/L
300 ng in 10 ml water		30,000 ng/L

Joudan et al also comments *"There was no apparent effort to determine whether the linear range of the calibration curve extended below this calibration standard."* As the lowest calibration standard is equivalent to 2 ng/L for a 1000 ml sample and the stated limit of detection is <1 ng/L, this is not necessary. **Joudan et al then incorrectly adds that** *"The authors define their LOD* [limit of detection] *and LOQ* [limit of quantification[17]] *based on their laboratory blanks, but the limited range of calibration standards indicate extrapolation was employed to quantify TFA in the blanks (as well as the samples)."* The lowest calibration standard is equivalent to 2 ng/L for a 1 litre snow sample. Von Sydow states that blank levels were always < 1 ng/L of TFA, and the limit of detection, defined as the average blank level plus three standard deviations of the blank, corresponded to 1 ng. **Joudan et al may have failed to recognize** that this and similar analytical procedures (concentrating the sample) were practiced at

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[17] Limit of quantification, LOQ stands for the smallest amount or the lowest concentration of a substance that is possible to be determined by means of a given analytical procedure with the established accuracy, precision, and uncertainty. For the Von Sydow paper the lowest calibration standard is appropriate for the measurements undertaken.

the time. More recent advance in instrumentation my allow for direct injection (hence less sample preparation would be needed).

Development of a fluorspar inventory

Fluorspar (CaF_2 mineral) is by far the dominant source of fluorine used by industry for a wide range of uses including production of fluorochemicals. Fluorspar production started to increase significantly in the mid-1930s[18] as the industries using fluorspar expanded. Fluorspar has three major uses: Hydrogen fluoride (HF) production, for fluorochemicals and aluminium production, steel production and a range of smaller uses.

EFCTC plans to develop an inventory to account, where possible, for the uses of fluorspar compared to production in the period 1930 to 1999. We firmly expect that this will confirm that the large burden of TFA in the oceans (61 – 205 million tonnes according to Scott) must include a large natural burden.

Conclusion

The fluorocarbons industry has funded wide ranging independent research to understand the environmental effects of TFA and anthropogenic TFA from HFCs and HFOs. This together with other independent research has enabled the Environmental Effects Panel for the Montreal Protocol to reach these conclusions in 2020.

In its Summary Update 2020 for Policymakers[19]**,** the UNEP Environmental Effects Assessment Panel has summarised these scientific conclusions for TFA: The current low concentration of trifluoroacetic acid (TFA) produced by the degradation of several hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs), is currently judged not to pose a risk to human health or to the environment. Trifluoroacetic acid continues to be found in the environment, including in remote regions, although concentrations are currently very unlikely to have adverse toxicological consequences for humans and ecosystems. While TFA is formed from the HFCs and HFOs regulated under the Montreal Protocol, a large amount of TFA was naturally formed over millions of years and has accumulated in the oceans. An unknown amount originates from fugitive emissions from chemical manufacture, waste disposal sites, laboratory use, and degradation of pharmaceuticals, pesticides, and industrial chemicals containing the trifluoromethyl group.

The case for a large natural burden of TFA in the oceans remains extremely strong and the proposed inventory of fluoride industrial uses is expected to support this. Even so, further research adding to the extensive literature on TFA should be encouraged.

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[18] British Geological Survey. 2014. World Mineral Production 2008–2012 Centenary Edition. Available at http://www.bgs.ac.uk/mineralsuk/statistics/worldStatistics.html

[19] available at Environmental Effects Assessment Panel (EEAP) | Ozone Secretariat (unep.org)

About EFCTC

The European FluoroCarbons Technical Committee is a Cefic Sector Group that monitors legislation related to HFCs (hydrofluorocarbons), and HFOs (hydrofluoro-olefins) in the EU and at global level.

Fluorocarbons are used as feedstock, as refrigerants, as solvents and as blowing agents for insulation plastic foams.

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